

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Allen A. Aradi	
Application No.: 10/696,618	Group Art Unit: 1797
Filing Date: October 29, 2003	Examiner: Cephia D. Toomer
Title: METHOD FOR REDUCING COMBUSTION CHAMBER DEPOSIT FLAKING	
Attorney Docket No.: NM 7607	

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

APPEAL BRIEF

Applicant submits this Appeal Brief following the Notice of Appeal that was
filed on January 16, 2008.

i. REAL PARTY IN INTEREST

The real party in interest is Afton Chemical Corporation, the assignee of the present application.

ii. RELATED APPEALS AND INTERFERENCES

There are no other appeals or interferences known to Appellant which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

iii. STATUS OF CLAIMS

Claims 1-28 are pending in the present application. At present, all of the claims are rejected. Applicant is appealing the rejection of all of the pending claims.

iv. STATUS OF AMENDMENTS

There are no amendments filed subsequent to the final rejection.

v. SUMMARY OF CLAIMED SUBJECT MATTER

The present invention is directed to a method of reducing combustion chamber deposit flaking and to reducing cold start emissions. Specifically, the present invention is directed to internal combustion engines that experience combustion chamber deposits and combustion chamber deposit flaking. Further, the internal combustion engine has an advanced emissions control.

Claims 1 and 15 are the two independent claims that are pending in the application. Turning first to claim 1, the method is directed to reducing combustion chamber deposit flaking in spark ignited internal combustion engines that experience combustion chamber deposits and combustion chamber deposit flaking. This discussion of the method is set forth at least on page 5, lines 1-10 of the application. The method further discloses supplying a fuel comprising additive that includes a metal-containing compound. This limitation is described at least at page 5, lines 5-18. The fuel is used in a spark ignited internal combustion engine having an advanced emissions control. This limitation is disclosed at page 5, line 19-page 6, line 5. Finally, the method includes the limitation that the metal-containing compound is supplied in an amount effective to reduce combustion chamber deposit flaking. This is disclosed at page 5, lines 11-18 and page 10, lines 17-23.

Claim 15 is directed to a method of reducing cold start emissions from spark ignited internal combustion engines that experience combustion chamber deposits and combustion chamber deposit flaking. This is discussed generally at page 11, lines 7-22 and page 14, lines 1-7. The method includes supplying a fuel comprising additive that include metal-containing compound. This is disclosed at page 5, line 11-17. The use of a spark ignited internal combustion engine having an advanced emissions control is disclosed at page 5, line 19-page 6, line 5. The final limitation is directed to a metal-containing compound being supplied in an amount effective to reduce cold start emissions. This is disclosed at page 14, lines 1-7.

Claims 12 and 26 are specifically directed to methods where the spark ignited internal combustion engine comprises a direct injection gasoline engine. This is disclosed specifically at page 5, line 18-page 6, line 1.

vi. GROUND OF REJECTION TO BE REVIEWED ON APPEAL

A. Claims 1-8, 13-22 and 27-28 are rejected under 35 USC §103(a) as being unpatentable over Dorer in view of Kalghatgi.

B. Claims 1-3, 6-10, 13-17, 20-24 and 27-28 are rejected under 35 USC §103(a) as being unpatentable over Henderson in view of Kalghatgi. Claims 11 and 12 are rejected under 35 USC §103(a) as being unpatentable over Henderson and Kalghatgi, and further in view of Kaneko.

C. Claims 12 and 26 are rejected under 35 USC §103(a) as being unpatentable over Dorer in view of Kalghatgi. Claims 12 and 26 are also rejected under 35 USC §103(a) as being unpatentable over Henderson in view of Kalghatgi.

vii. ARGUMENT

A. Claims 1-8, 13-22 and 27-28 are patentable
over Dorer in view of Kalghatgi.

Neither the Dorer reference nor the Kalghatgi reference is entitled to the breadth of disclosure necessary to justify a rejection of the above-referenced claims. The sum of the references does not equal the claimed invention. In fact, those references teach away from the present invention. Also, the rejection does not define a person of

ordinary skill in the art; however, a properly identified such person would not find the purported combination obvious.

1. The Dorer disclosure does not teach that metal compounds function as detergents that reduce combustion chamber deposits.

In order for the current rejection based on Dorer to be effective, the statement that the Dorer reference teaches a metal detergent must be true. That is, the Dorer composition must reduce engine deposits. Because this is not true, the rejection must be reversed.

Turning to the Dorer reference, Applicant notes that the rejection states that "Dorer teaches that the fuel additive of his invention reduces engine deposits (see column 1, line 50-55)." Applicant respectfully submits that this conclusion is not entirely correct. Applicant sets forth herein an excerpt from Dorer that includes the specific passage cited in the rejection as referenced above.

Manganese and copper compounds are both effective in reducing the ignition temperature of diesel engine exhaust particulate. Copper compounds, however, are more effective ignition temperature reducers than manganese compounds. While copper compounds are very effective ignition temperature improvers, their use can result in engine deposits. In accordance with the present invention, it has now been found that the ignition temperature reduction and propagation of the burning of exhaust particulate from internal combustion engines, particularly diesel engines, is improved along with a reduction in engine deposits. (Column 1, Lines 43-55).

The above-referenced passage is relied upon as teaching that the Dorer composition actually reduces engine deposits. Instead, more correctly read, Dorer states that while copper compounds alone are better combustion improvers, the use of copper

compounds can result in engine deposits. Therefore, according to Dorer, it is possible to obtain the beneficial results of a combustion improver by using less copper but combining the copper with manganese. See, e.g., Abstract. The result of using less copper is that less engine deposits are formed. In other words, there is no reduction in engine deposits as a result of the Dorer composition, and there is no expectation, teaching, suggestion or motivation of the presently-claimed invention. Instead, less deposit is actually formed, because less copper compound is used.

The rejection requires that the metal compounds of Dorer function as “detergents” to reduce deposits; however, Applicant submits that any person of skill in the art recognizes that a “detergent” in the context of fuel additives means a composition that actually decreases an amount of existing deposits. Therefore, a detergent not only prevents the formation of deposits, it reduces the amount of existing deposits. This definition of detergent is contrary to the above-referenced passage in Dorer that merely stands for the proposition that fewer deposits are formed (due to decreasing use of copper)--not that any deposits are actually removed by a detergent.

Because Dorer does not disclose a detergent and does not otherwise reduce any existing deposits, the rejection must be reversed. This strained link to Kalghatgi is not supported.

2. The complete disclosure of Kalghatgi teaches away from the present invention. Kalghatgi does not teach that all detergent additive packages make combustion chamber deposits less likely to flake.

All of the rejections require that Kalghatgi stands for the proposition that conventional detergent additive packages make combustion chamber deposits less likely to flake. Without this essential assumption, the rejections of the present claims in view of the combination of Kalghatgi with either Dorer or Henderson are traversed.

Applicant believes that the complete teaching of Kalghatgi does not include any statement that all detergents reduce deposit flaking. On the contrary, Kalghatgi demonstrates the nonobviousness of the present invention and is a corroborating summary of the testimony of Allen Aradi in his early-submitted declaration. Applicant calls the Board's attention to the "Conclusions" of Kalghatgi set forth at the end of the SAE Paper. A copy is attached as Exhibit 2. Applicant submits that conclusions number 2, 3 and 5 of Kalghatgi are all relevant to teaching away from the present invention and away from any conclusion about detergents all reducing flaking. Accordingly, Kalghatgi in fact stands for the fact that the present invention is unexpected. Kalghatgi is inappropriate for combination with either Dorer or Henderson as articulated in the rejection. Each relevant Kalghatgi conclusion will be discussed separately.

Conclusion Number 2: There is a wide variation between different fuels and additives. Conventional detergent additive packages suppress flaking whereas some experimental additives can promote flaking.

As explained in the article, the “conventional” detergent packages used in Kalghatgi are set forth in Table 2 of Kalghatgi. These conventional packages include a polyether detergent- -AD 6. The other, experimental additive compositions include a polyether detergent (AD 3) as well as additive packages that include polyether amides (AD 7 - AD 10). Therefore, the conclusion number 2 of Kalghatgi is not that every detergent is inherently able to suppress combustion chamber deposit flaking. On the contrary, Kalghatgi only stands for the proposition that five (5) of the detergent additives that were tested suppress flaking while other detergent additive packages may actually promote flaking. Therefore, it is improper to conclude that Kalghatgi teaches that all detergents will suppress flaking. Kalghatgi clearly stands for the proposition that just the opposite is true.

Conclusion Number 3. Deposition flaking depends on the temperature regime under which the deposits are formed. Thus fuels which might produce deposits which do not flake in one engine (or operating regime) might produce deposits which flake in another engine (or operating regime) with a different thermal environment.

Applicant has represented and argued in earlier responses that different engine types, including specifically the claimed engine types having advance emissions control, may have different combustion chamber flaking problems from other engine types. The conclusion of Kalghatgi explicitly reinforces and scientifically endorses this view that not all engines operate the same. Not all combustion chamber deposits flake the same. In fact, these deposits will flake in different ways in different thermal environments which includes different types of engines.

This conclusion of Kalghatgi, therefore, does not support the broad assumption that is a foundation of the rejections. Instead, this conclusion points out the fact of flaking that broad assumptions cannot be made. For instance, engine types can and do affect levels of flaking. An unsupported combination with Dorer (or Henderson) is unfair and contrary to common sense.

Conclusion 5. There is no correlation between the deposit level i.e. weight or thickness and the susceptibility to flake.

This statement regarding the fact that combustion chamber deposit flaking is not necessarily directly correlated with the amount of deposits is a direct endorsement of Applicant's arguments. In other words, the present invention is not directed to the formation or lack thereof of combustion chamber deposits. The present invention is directed to reducing flaking of those deposits. In the rejection, there is the following statement: "Dorer and Henderson specifically teach that the metal compounds do inhibit deposits and the skill artisan having a spark-ignited combustion engine having an advanced emissions control would have every expectation that the composition of Henderson and Dorer would reduce deposit flaking in the combustion chamber, *especially in view of the teachings of Kalghatgi.*" (Page 7 of Office Action, emphasis added.) Applicant submits that this statement of the rejection is explicitly refuted by the foregoing conclusion of Kalghatgi that there is no fair correlation between deposits and flaking.

In summary, when considering all of the teachings of Kalghatgi, it is undisputable that the assumptions underlying the rejections about detergents and

flaking generally are incorrect. For this reason alone, the current rejections should be reversed.

3. There is no justification for the combination of Dorer and Kalghatgi other than hindsight.

In the most recent rejection, it is admitted that Dorer does not disclose the methods of claims 1 and 15--the independent claims from which all of the other above-referenced claims are dependent from. In fact, just to be perfectly clear, Dorer nowhere mentions combustion chamber deposit flaking. Aside from the sole passage set forth above, Dorer does not mention engine deposits. There are no experimental results that relate to combustion chamber deposits. There is no teaching or other disclosure with respect to the separate physical events and concepts of combustion chamber deposit flaking and combustion chamber deposit formation. There is no justification, either based on common sense or any other scientific basis, that entitles the combination of Dorer and Kalghatgi to arrive at the claimed invention.

The sum of Dorer and Kalghatgi simply does not equal, and cannot equal, the claimed invention. The undisputed evidence of record in the attached Aradi declaration explains this very clearly. There must be combustion chamber deposits in order to be possible to have combustion chamber deposit flaking. However, just because an engine has combustion chamber deposits, does not mean that it will experience flaking of those deposits. It is undisputed that it is possible to have relatively little combustion chamber deposit mass but still have a flaking problem. Likewise, it is possible to have a relatively large amount of combustion chamber deposit

with only a minor or no flaking problem. The present invention is directed to reducing flaking and improving cold start emissions without regard to the amount of combustion chamber deposits. The only way to join Dorer and Kalghatgi is to arbitrarily, with hindsight, distort the disclosures of Dorer and Kalghatgi and then, without adequate explanation, join them together to try to equal the claimed inventions.

4. The rejection does not identify the hypothetical person of ordinary skill in the art.

The obviousness rejection based on the combination of Dorer and Kalghatgi (and further based on the combination of Henderson and Kalghatgi) requires that a hypothetical person of ordinary skill in the art finds the present invention obvious in view of the referenced combinations. Nowhere is this person of ordinary skill identified. Therefore, applicant is unable to sufficiently rebut the characterization of this person and the alleged combination. On the contrary, the Aradi Declaration that is attached specifically defines a person of ordinary skill in the art and explains that that person of ordinary skill would not find the present invention obvious without the benefit of hindsight and disclosure of the present patent application. See paragraph 6 of the Aradi Declaration. This definition of a person of ordinary skill in the art is unrebutted. Therefore, the rejections must be reversed in view of this undisputed definition of the person of ordinary skill.

As explained, a person of ordinary skill in the art of gasoline formulations is not historically aware of the problems of combustion chamber deposit flaking or cold start emissions. This person of ordinary skill in the art is only recently aware of the flaking

problem and the resulting cold start emissions problems as a result of the use of advanced emissions controls or direct injection gasoline engines. If the person of ordinary skill in the art had been aware of flaking problems prior to these modern engines, then it would have been reported. Therefore, applicant believes that it is not possible to arrive at the present invention without the teachings and the map of the present disclosure.

For at least the foregoing reasons, Applicant submits that claims 1-8, 13-22 and 27-28 are patentable over Dorer in view of Kalghatgi. Applicant requests that the foregoing rejection be reversed.

- B. Claims 1-3, 6-10, 13-17, 20-24 and 27-28 are
patentable over Henderson in view of Kalghatgi.

Many of the same problems that exist with respect to the earlier rejection discussed herein are likewise flawed with respect to the rejection of the foregoing claims based on the combination of Henderson and Kalghatgi. The shortcomings of the Kalghatgi reference are documented above. Contrary to the arguments of the rejection, Henderson is not taught to be any type of detergent. The combination of Henderson and Kalghatgi does not equal the claimed invention.

1. The Henderson reference does not teach that the compositions therein serve as a detergent that reduces combustion chamber deposits.

The rejection requires that the composition in Henderson prevents combustion chamber deposits. This is an incorrect restatement of the disclosure of Henderson. Specifically, the passage cited by the Office Action reads as follows:

It is a further object of the invention to increase the detonation resistance of gasolines containing such additives without increasing either the toxicity of the fuel compositions or its tendency to lay down combustion chamber deposits. (Henderson, Column 2, Lines 15-19).

In other words, the proper statement of the disclosure of Henderson is that the gasolines disclosed in Henderson do not reduce combustion chamber deposits.

Henderson merely states that the Henderson invention does not increase the tendency to lay down combustion chamber deposits. This means that combustion chamber deposits will still be formed. There is simply no increase in the tendency to lay them down. Henderson does not stand for any reduction or elimination of the formation of combustion chamber deposits.

Because Henderson does not teach a reduction of deposits, the rejection on the basis of Henderson reducing deposits must be reversed.

2. The complete disclosure of Kalghatgi teaches away from the present invention.

Applicant repeats and realleges its earlier arguments set forth in section A.2 above with respect to the shortcomings and failures of disclosure of Kalghatgi. Kalghatgi does not stand for the broad proposition that all detergents reduce flaking. Applicant reemphasizes that Kalghatgi in fact reinforces the arguments of Applicant with respect to the flaking issues. Because of these failures in disclosure, the rejection must be reversed.

3. The combination of Henderson and Kalghatgi does not equal the present invention.

As explained above, the actual disclosure and teachings of Henderson undermine the present rejections. Henderson does not teach that metal compounds would inhibit the formation of combustion chamber deposits. Further, there is no teaching or other disclosure in Henderson with respect to the separate and different concept of flaking of deposits. Therefore, the combination of the completely unrelated Henderson and Kalghatgi references is not justified or justifiable.

For any one or more of the foregoing reasons, Applicant requests that the rejection of claims 1-3, 6-10, 13-17, 20-24 and 27-28 be reversed. Favorable action is requested hereon.

4. The person of ordinary skill in the art has not been identified in the rejection.

For all the reasons set forth earlier in connection with Section A.4., applicant respectfully requests that the rejection, based on the combination of Henderson and Kalghatgi be reversed. No person of skill in the art would combine Henderson and Kalghatgi to obtain the present invention.

- C. Neither Dorer nor Henderson in combination with Kalghatgi is sufficient to disclose and therefore justify the rejection of claims 12 and 26.

Claims 12 and 26 are directed to direct injection gasoline (DIG) engines.

Therefore, the environment of this claimed invention is very specific. The current rejections of these claims are based on the broad assumption that the DIG engine is an

internal combustion (IC) engine, so the teachings in Dorer and Henderson of IC engines should automatically apply to DIG engines as well. This is simply not true.

The Declaration of Aradi specifically discusses the historical onset of the problems relating to combustion chamber deposit flaking. This phenomenon has recently become an issue in the context of direct injection gasoline engines. As explained, the flaking and cold start problems were not recognized before the modern technology that includes direct injection gasoline engines. Therefore, it evident that these specific types of combustion systems are prone to the problems solved by the present method. Likewise, as discussed earlier herein, Kalghatgi explicitly teaches that different engines may have different or no flaking issues -- see Kalghatgi conclusion number 3.

The rejection directed to claims 12 and 26 merely groups together all spark ignited internal combustion engines and direct injection gasoline engines. The rejections specifically state that they are justified absent evidence to the contrary. Applicant submits that the Declaration of Allen Aradi and the Kalghatgi article are that undisputed evidence to the contrary that has not been recognized.

For at least one or more of the foregoing reasons, Applicant submits that claims 12 and 26 are allowable. Applicant requests that the rejection be reversed.

CONCLUSION

For any one or more of the foregoing reasons, applicant submits that all of the claims 1-28 are in condition for allowance. Favorable action is requested hereon.

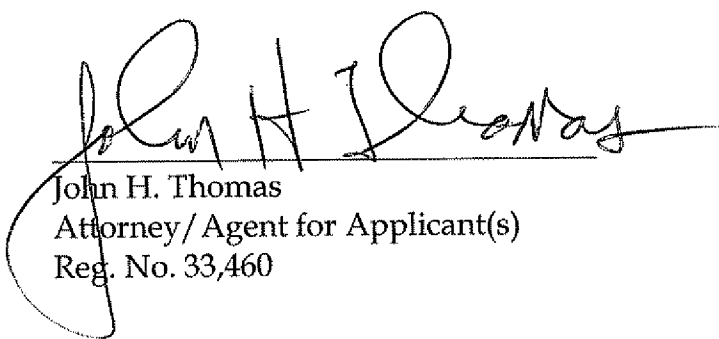
The Commissioner is hereby authorized to charge any deficiencies in payment of the following fees associated with this communication or credit any overpayment to Deposit Account No. 50-2127.

Respectfully Submitted,

Date: February 25, 2008

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viii. Claims Appendix

1. A method of reducing combustion chamber deposit flaking in spark ignited internal combustion engines that experience combustion chamber deposits and combustion chamber deposit flaking comprising the steps of:

supplying a fuel comprising an additive that includes a metal-containing compound to a spark ignited internal combustion engine having an advanced emissions control,

wherein the metal-containing compound is supplied in an amount effective to reduce combustion chamber deposit flaking.

2. A method as described in claim 1, wherein the metal-containing compound comprises a metal selected from the group consisting of manganese, platinum, palladium, rhodium, iron, cerium, copper, nickel, silver, cobalt, and molybdenum, and mixtures thereof.

3. A method as described in claim 2, wherein the metal-containing compound comprises a manganese-containing compound.

4. The method described in claim 3, wherein the manganese-containing compound is an inorganic manganese compound.

5. The method described in claim 4, wherein the inorganic manganese compound is selected from the group consisting of fluorides, chlorides, bromides, iodides, oxides, nitrates, sulfates, phosphates, nitrides, hydrides, hydroxides, carbonates and mixtures thereof.

6. The method described in claim 3, wherein the manganese-containing compound is an organometallic compound.

7. The method described in claim 6, wherein the organometallic compound is selected from the group consisting of alcohols, aldehydes, ketones, esters, anhydrides, sulfonates, phosphonates, chelates, phenates, crown ethers, carboxylic acids, amides, acetyl acetonates and mixtures thereof.

8. The method described in claim 3, wherein the manganese-containing compound comprises about 1 to about 50 mgMn/liter of the fuel.

9. The method described in claim 6, wherein the organometallic compound comprises methylcyclopentadienyl manganese tricarbonyl.

10. The method described in claim 3, wherein the manganese-containing compound is selected from the following group: cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl

manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, tetramethylcyclopentadienyl manganese tricarbonyl, pentamethylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, diethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, tert-butylcyclopentadienyl manganese tricarbonyl, octylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and the like, including mixtures of two or more such compounds.

11. A method as described in claim 1, wherein the fuel contains less than about 30 ppm of sulfur.

12. The method as described in claim 1, wherein the spark ignited internal combustion engine comprises a direct injection gasoline system.

13. The method as described in claim 1, wherein the fuel comprises regular, unleaded gasoline.

14. The method as described in claim 1, wherein the engine comprises six or more cylinders.

15. A method of reducing cold start emissions from spark-ignited internal combustion engines that experience combustion chamber deposits and combustion chamber deposit flaking comprising the steps of:

supplying a fuel comprising an additive that includes a metal-containing compound to a spark ignited internal combustion engine having an advanced emissions control;

wherein the metal-containing compound is supplied in an amount effective to reduce cold start emissions.

16. A method as described in claim 15, wherein the metal-containing compound comprises a metal selected from the group consisting of manganese, platinum, palladium, rhodium, iron, cerium, copper, nickel, silver, cobalt, and molybdenum, and mixtures thereof.

17. A method as described in claim 16, wherein the metal-containing compound comprises a manganese compound.

18. The method described in claim 17, wherein the manganese-containing compound is an inorganic manganese compound.

19. The method described in claim 18, wherein the inorganic manganese compound is selected from the group consisting of fluorides, chlorides, bromides,

iodides, oxides, nitrates, sulfates, phosphates, nitrides, hydrides, hydroxides carbonates and mixtures thereof.

20. The method described in claim 17, wherein the manganese-containing compound is an organometallic compound.

21. The method described in claim 20, wherein the organometallic compound is selected from the group consisting of alcohols, aldehydes, ketones, esters, anhydrides, sulfonates, phosphonates, chelates, phenates, crown ethers, carboxylic acids, amides, acetyl acetonates and mixtures thereof.

22. The method described in claim 17, wherein the manganese-containing compound comprises about 1 to about 50 mgMn/liter of the fuel.

23. The method described in claim 20, wherein the organometallic compound comprises methylcyclopentadienyl manganese tricarbonyl.

24. The method described in claim 17, wherein the manganese-containing compound is selected from the following group: cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, tetramethylcyclopentadienyl manganese tricarbonyl, pentamethylcyclopentadienyl

manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, diethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, tert-butylcyclopentadienyl manganese tricarbonyl, octylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and the like, including mixtures of two or more such compounds.

25. A method as described in claim 15, where the fuel contains less than about 30 ppm of sulfur.

26. The method as described in claim 15, wherein the spark ignited internal combustion engine comprises direct injection gasoline system.

27. The method as described in claim 15, wherein the fuel comprises regular, unleaded gasoline.

28. The method as described in claim 15, wherein the engine comprises six or more cylinders.

ix. EVIDENCE APPENDIX

1. Declaration of Allen A. Aradi executed 11/17/2006.

2. Article by Kalghatgi, G.T and Price, R.J., *Combustion Chamber Deposit Flaking*, SAE 2000-01-2858..

x. RELATED PROCEEDINGS APPENDIX

None.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Allen A. Aradi Application No.: 10/696,618 Filed: 10/29/2003 Title: METHOD FOR REDUCING COMBUSTION CHAMBER DEPOSIT FLAKING Attorney Docket No.: EI 7607	Group Art Unit: 1714 Examiner: Cephia D. Toomer
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Commissioner of Patent
P.O. Box 1450
Alexandria, Virginia 22313-1450

Declaration Of Allen A. Aradi

I, Allen A. Aradi, declare as follows:

1. I am an Advisor, in the Fuels Research and Development division at Afton Chemical Corporation, the assignee of the present patent application. I have been employed by Afton Chemical or its predecessor in interest for 16 years. I have and have had personal involvement with research and development in the field of fuel additives including knowledge of related fuel combustion systems.

2. Combustion chamber deposit flaking in spark ignition engines is not the same subject as the existence of combustion chamber deposits. There will be no deposit flaking if there are no combustion chamber deposits in an engine. However, the amount of flaking that occurs in an engine may vary

regardless of the amount or mass of combustion chamber deposits in an engine. For example, an engine may have a relatively low mass of combustion chamber deposits but still have a relatively high amount of combustion chamber deposit flaking. Likewise, an engine may have a relatively high mass or amount of combustion chamber deposits and a relatively low amount of or no detectible combustion chamber deposit flaking.

3. Combustion chamber deposit flaking is not related to the issue of reducing combustion chamber deposits. In a normal spark ignition engine, combustion chamber deposits may increase or decrease in the ordinary operation of the engine. Typically, the reduction in combustion chamber deposits is a result of the combustion of some of the deposit mass during the combustion of the fuel within an engine cylinder. To the extent that there exists historical knowledge with respect to reducing or controlling the amount of combustion chamber deposits, that science or understanding is unrelated to the phenomenon of combustion chamber deposit flaking.

4. Combustion chamber deposit flaking is a problem that was not recognized or reported before the availability of advanced emissions controls systems. Likewise, combustion chamber deposit flaking has recently become an issue in the context of direct injection gasoline engines. If combustion chamber deposit flaking had been a problem before the introduction of these modern engine technologies, then that flaking would have been recognized and

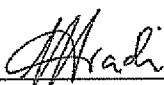
reported. Since I am not aware of any recognition or other reporting with respect to deposit flaking before the modern technology, then I believe that it is reasonable to assume that combustion chamber deposit flaking was either insignificant or did not occur at all until the advent of the modern technology.

5. The subject and phenomenon of combustion chamber deposit flaking is not associated with the general subject matter of internal combustion engines broadly speaking. Combustion chamber deposit flaking is solely recognized in the context of internal combustion engines having advanced emissions control systems or other modern systems such as direct injection gasoline systems.

6. I believe that a person of ordinary skill in the art of the present invention is knowledgeable with respect to gasoline formulations. This person of ordinary skill has a relatively low knowledge with respect to the problem of combustion chamber deposit flaking. The person of ordinary skill in the art would have no knowledge at all with respect to combustion chamber deposit flaking prior to the introduction of advanced emissions control systems. I believe that the present invention would not be obvious to this person of ordinary skill in the art without the benefit of hindsight and disclosure of the present patent application.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 11/17/06


Allen A. Aradi

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PAPER SERIES**

2000-01-2858

Combustion Chamber Deposit Flaking

G. T. Kalghatgi and R. J. Price
Shell Global Solutions

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Combustion Chamber Deposit Flaking

G. T. Kalghatgi and R. J. Price
Shell Global Solutions

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ABSTRACT

There is increasing concern that small flakes of combustion chamber deposits (CCD) can break loose and get trapped between the exhaust valve and the seat resulting in difficulties in starting, rough running and increase in hydrocarbon emissions. In this paper we describe experimental observations which might explain how this flaking of CCD occurs and the factors that might be important in the phenomenon. The experiments include thirty one engine tests as well as tests done in a laboratory rig and show that some CCD flake when they are exposed to water; indeed water is far more effective in bringing this about than gasoline or other organic solvents. The hydrophilicity of the deposit surface which determines the penetration of water and the inherent susceptibility of the relevant deposit layer to interact with water are both important. Consequently there are large differences between deposits produced by different fuels and additives in terms of their susceptibility to flake. In general the use of conventional detergent additive packages makes the CCD less likely to flake. The age and thermal history of deposits also has an important impact on deposit flaking.

1. INTRODUCTION

Combustion chamber deposits (CCD) build up in all gasoline engines with use and can affect engine performance and emissions in different ways (1). More recently a new problem associated with CCD has been identified. There is increasing concern that small flakes of CCD can break loose and become trapped between the exhaust valve and the seat. This can result in difficulties in starting, rough running and increase in hydrocarbon emissions.

This problem appears only in cars which have accumulated some deposits and, usually, only if the car has been driven a very short distance with no chance for the engine to warm up and then parked for some time e.g. overnight. In some cases deposits are believed to flake during this period. When a restart is attempted, one or more cylinders might misfire and in the worst case the engine might not start at all. This is ascribed to one or more exhaust valves not sealing properly because of

deposit flakes trapped between the valve and the valve seat. This leads to loss of compression and would also cause increased hydrocarbon emissions because of leakages of unburned mixture. It is felt that as on-board diagnostic (OBD) systems become more widely used this problem will become more readily recognised.

Deposit flaking could occur locally during engine operation due to thermal stresses and in some engine experiments abrupt increases in wall temperature have been noted and have been attributed to such flaking (2,3). However in our experience (4) when in-situ measurements of deposit thickness are made, such flaking is rarely found. In fact abrupt thinning of deposits, when it was observed, was usually seen after cold starts rather than during engine operation (4). It is much more likely that some times deposits lose their structural integrity during the time the engine is not running and are much more likely to flake off when the engine is restarted.

It is common knowledge amongst people who frequently dismantle engines in service garages that, occasionally, if a combustion chamber surface with deposits is left exposed to the atmosphere over some time, say overnight, deposits lift off the metal surface. If the engine were to be restarted with the deposits in such a state, one of these flakes could become trapped on the exhaust valve seat. In this paper we describe experimental observations on such flaking of combustion chamber deposits and the factors that might be important in this phenomenon. These observations show that water is a very effective agent to bring about deposit flaking.

2. EXPERIMENTAL OBSERVATIONS

The observations described in this paper are from two different series of experiments - a four cylinder research engine and a laboratory rig. These will be described separately. Properties of the base fuels used are listed in Table 1 and the additives used are listed in Table 2. Of these AD1, AD2, AD4, AD5 and AD6 are detergent additive packages which have been or are being used commercially. The others are experimental additives.

2.1. EXPERIMENTS IN A FOUR-CYLINDER RESEARCH ENGINE - These experiments were conducted in a 1.6 L VW engine modified for research and were primarily done to study CCD growth and the effects of CCD on knock and fuel consumption as described in previous publications (e.g. 5,6,7). CCD weights and thicknesses were monitored on removable plugs carried in the slice between the head and the block. Figure 1 is a plan view of Cylinder 1 showing the different measurement locations.

The deposits were built up with the engine running at 2250 rev/min with a load of 30 Nm. The engine was stopped every 15-20 hours and allowed to cool down. At these intervals the plugs were removed and deposit weights and mean thicknesses at each of four locations, A, B, C and D (Figure 1) were determined. Of these locations, A is at the tip of the probe while B, C and D are

in the squish area with the surface temperature decreasing as one moves towards the chamber wall from B to D (Figure 1). Surface temperatures are higher for the plug near the exhaust valve compared to the plug near the inlet valve. The average surface temperatures at these locations, at the deposit acquisition conditions have been measured to be as follows (4) - 220° C at A, 256° C at B, 226° C at C and 188° C at D. The probe tips (A) are probably cooled by the impinging inlet flow and hence are at a lower temperature than at B.

The deposits were built up with the engine running usually for 90 hours with six cold starts; the plugs were removed and measurements made during these stops. At the end of the test the engine was dismantled and many of the further tests on deposit flaking discussed below were carried out.

TABLE 1
PROPERTIES OF THE BASE FUELS USED

	FUEL E	FUEL F	FUEL G	FUEL H	FUEL I
RON	100	98.3	98.5	88.8	95.3
MON	88.5	87.1	88.7	81	84.7
Density, gm/ml	0.791	0.773	0.768	0.744	0.737
RVP, mbar	723	739	647	570	695
Aromatics, %v	57.1	45.6	50.1	19.6	30.8
Olefins, %v	4	9.2	0.4	17.5	6.74
Saturates, %v	38.9	45.2	49.4	63	48
MTBE, %v	0	0	0	0	13.8
unwashed gum, mg/100ml	14	4	3	5	1
washed gum, mg/100ml	1	<1	<1	<1	<1
Total Sulphur, ppmw	123	193			7
IBP, C	31	33	21.6	32.5	34
E70, %v	14	21	24.3	19.5	32
E100, %v	28	41	43.1	35.5	59
E150, %v	80	82	79.8	71	91
E180, %v	96	96	96	90	100
FBP, C	211	200	196	206	177

TABLE 2
LIST OF ADDITIVE PACKAGES USED IN THE TESTS

CODE	DESCRIPTION
AD1	Additive package, 1300 ppmw. PIB succinimide detergent + mixture of carriers
AD2	Additive package 1300 ppmw. PIB EDTA detergent + mixture of carriers
AD3	500 ppmw polyether detergent.
AD4	Additive package 1100 ppmw. PIB amine detergent + carrier
AD5	Additive package 900 ppmw. PIB amine detergent + carrier
AD6	Additive package. Polyether detergent
AD7	Experimental additive 1250 ppmw. Polyether amide derivative 1
AD8	Experimental additive package 875 ppmw. Polyether amide derivative 2 + synthetic
AD9	Experimental additive 625 ppmw. Polyether amide derivative 3
AD10	Experimental additive 500 ppmw. Polyether amide derivative 4.

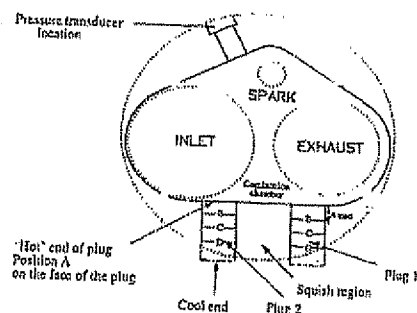


Figure 1 Slice layout plan viewed from piston side for Cyl.#1 showing plug positions

2.1.1 Preliminary qualitative observations of deposit flaking - One of the tests (Test #21) was run in three stages - 90 hours on Fuel E, followed by 45 hours on Fuel E containing an experimental additive and finally, 60 hours on Fuel E with 0.5%v methyl propanol. About 24 hours after the end of Test #21, the engine was dismantled.

- a. Significant deposit flaking was noticed in the head and the slice, particularly on the squish surfaces; large (5mm x 3mm) areas of deposit had lifted off the metal in the squish areas. There were large areas where deposits had disappeared and clean metal could be seen. This was particularly noticeable in cylinders 2,3 and 4 which had one of the valves open so that during the previous 24 hours, the deposits had been exposed to air and the moisture in the air. We had not seen such extensive flaking across the whole of the combustion chamber in previous experiments.
- b. We put a small drop of water on the smooth deposit in the squish area of cylinder 1 where the deposit was firmly attached to the metal. About 15 minutes later, this area had "bubbled" up and the deposit could be removed by blowing lightly on it.
- c. We observed this effect several times by placing drops of water on the deposits on the piston surfaces. After around 10 minutes, the deposit surface in the region where the water drop is located very suddenly "bubbled" up, sometimes with enough violence for small chunks of material to lift several centimetres off the surface. Water disappears below the surface through the cracks in the deposit and these cracks continue to propagate in sudden bursts for a further 10 minutes or so.
- d. We sprayed water on the tops of two of the pistons which were covered with deposits. About 15 minutes later a large fraction (about 70%) of the deposit surface had lifted off the surface and could be removed simply by lightly blowing on it. The smooth deposits in the cooler half of the piston, on the inlet valve side were much more susceptible to this effect

than the deposits in the exhaust valve side which were rougher and more mottled. Similarly, deposits in the head which generally has cooler surface temperatures compared to the piston were more susceptible to this effect e.g. piston-top deposits had not flaked simply by coming into contact with (humid) air unlike head deposits.

- e. We tried coating piston-top deposits with various other materials - isobutyl alcohol, n-heptane, jeffamine ED 970, Jeffamine in gasoline (2000 ppm), polyethylene glycol (PEG) and mono ethylene glycol (MEG). Water was by far the most effective agent for inducing flaking.

2.1.1.1 Test #22: - In Test 22 the engine was run for 90 hours on Fuel E followed by 49 hours on base fuel containing the same experimental additive used in the second stage of Test #21 and the head was taken off.

- a. Once again we placed drops of water on various deposit surfaces. There was some deposit flaking but it took nearly 40 minutes for this to happen and the events were nowhere as extensive or as violent as after Test 21. Clearly these deposits were less susceptible to flaking compared to Test 21
- b. We wiped some areas lightly with a very dilute solution of washing-up liquid in water (couple of drops in a cup of water) and then placed a drop of water on each of these areas. The water wet the surface instead of sitting as a drop. Deposits in these areas flaked violently in around six minutes (as opposed to 40 minutes in areas not wiped with washing-up liquid solution).

2.1.1.2 Test #23 - In this test the engine was run for 111 hours on Fuel E with the non-commercial experimental additive AD10. The engine was dismantled after about 72 hours after the end of the test and the head removed exposing the piston crowns. It was left in the test cell for about three hours prior to flaking experiments.

Each of the four piston heads was sprayed with a different liquid. The temperature in the test cell was about 20° C and the atmosphere was humid. This may be similar to the conditions present when the engine is cooling down and not running (typically three out of four cylinders will be open to the atmosphere in a static engine). The four liquids tested on the piston heads were:

Water alone; gasoline containing polyethylene glycol (PEG) at about 2% using washing-up liquid as an emulsifier; gasoline containing monoethylene glycol (MEG) at about 2% using washing-up liquid as an emulsifier; and gasoline alone.

The experiments were carried out on two days and as a consequence the engine was left exposed to the atmosphere overnight. Figure 2 shows the 4 pistons prior to experiment.

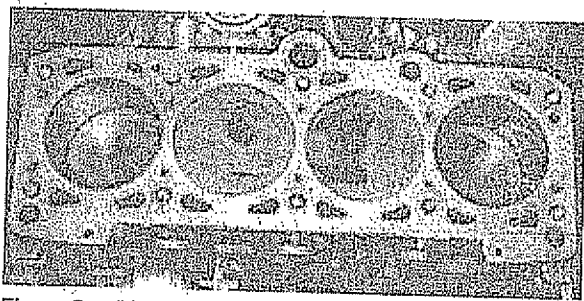


Figure 2. Piston tops after Test #23 before experiments with water

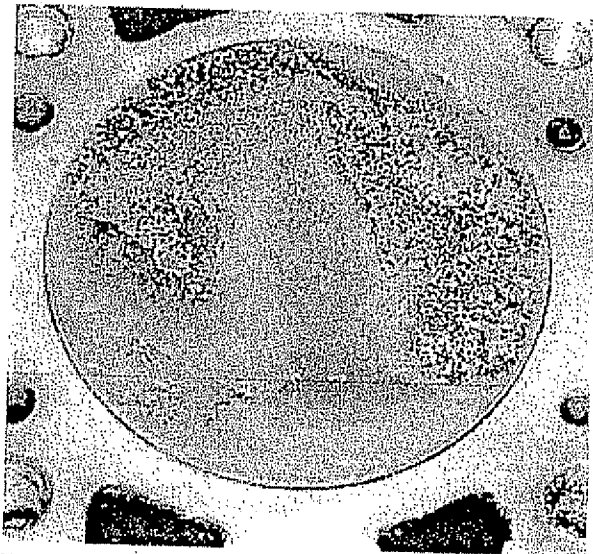


Figure 3. Piston top (Cylinder #4) at the end of Test #23 before water was sprayed.

Coating with water.

A photograph was taken to record the appearance of the piston top in cylinder 4 before testing involving coating with water began, Figure 3. Initially, one drop of water was placed on the piston top which remained at the point of application. Several minutes later the water ran down the piston top (the piston top is slightly inclined to the horizontal). After 6 minutes there was a very noticeable lifting of the deposits in the area that had been touched by the water. Some deposit spontaneously flew off the piston top, probably due to release of stress within the deposit.

Eventually water had been applied to the entire deposit surface. Within 40 minutes the deposits across the entire piston head had cracked and lifted from the surface. At this point when water was sprayed it simply soaked

underneath the cracked deposit straight away. The piston was then left overnight, after which there had been some further flaking of the deposit, although the majority of lifting had already taken place within the first hour. A photograph was taken to record the appearance of the piston top in cylinder 4 at this stage, Figure 4. The deposit was then removed by blowing gently across the top of the piston head and a further photograph taken,

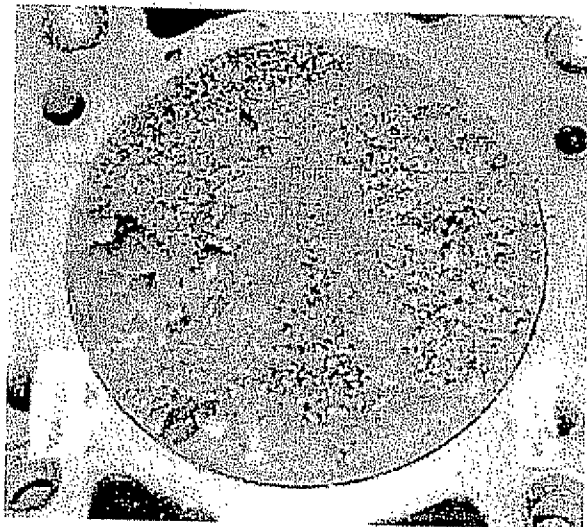


Figure 4. Piston top (Cylinder #4) at the end of Test #23 after water had been sprayed

Application Of Gasoline & PEG, Gasoline Only and Gasoline & MEG:

When these liquids were applied to the piston top, they tended to spread over the deposit surface and evaporate. For the first 30 minutes coating with the liquid was repeated immediately after the previous liquid had evaporated. Some lifting of the deposit was noticeable after 25 minutes but nowhere to the extent found with water. The liquid was reapplied several more times and then left overnight. More flaking could be observed the next day. It is very likely that the deposits absorbed moisture from the atmosphere overnight. Figure 6 shows the piston-top of cylinder #3 at the end of the coating experiments using gasoline and MEG and comparison with Figure 5 shows that water is much more effective in bringing this effect about.

Experiments On The Cylinder Heads:

Similar experiments were carried out on the cylinder heads in the areas surrounding the inlet and exhaust valves. Again water was found to be the most effective agent in bringing about this effect.

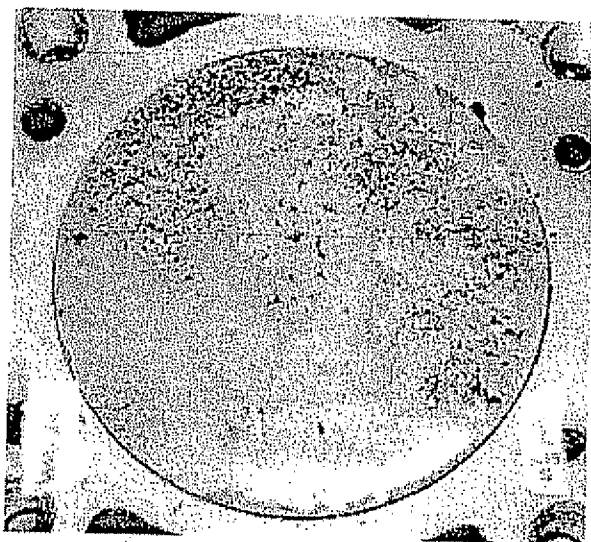


Figure 5. Piston top (Cylinder #4) at the end of Test #23 after water had been sprayed and deposits removed by blowing.

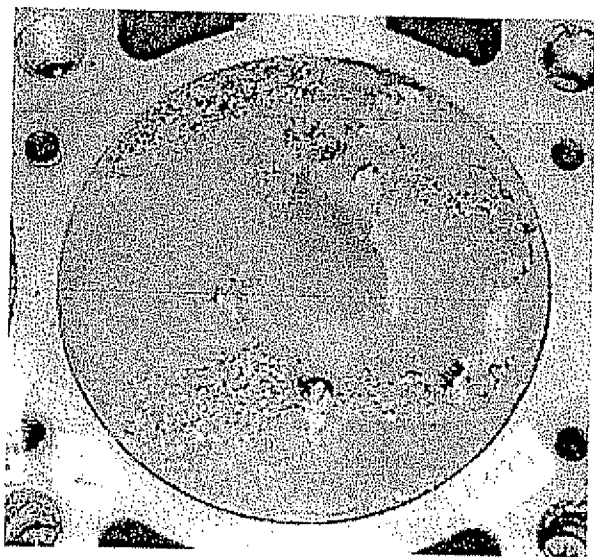


Figure 6. Piston top of cylinder #3, Test #23 after spraying with gasoline and MEG and blowing to remove flakes. There is far less flaking compared to Fig. 5.

2.1.1.3 Test #24 – This test was run on Fuel E on its own for 105 hours. The engine was dismantled about 75 hours after the end of the test. By the time that the first set of photographs of the piston heads were taken, the piston heads had been exposed to the atmosphere for a further four hours.

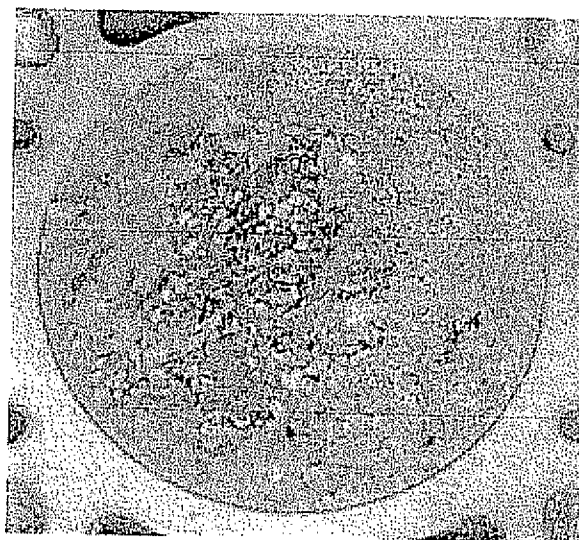


Figure 7. Piston-top of cylinder #2 after Test #25 showing spontaneous flaking of CCD through absorption of ambient water vapour. Other cylinders showed similar flaking. The engine was dismantled 20 hours after the end of the test.

Thus the deposits had a lot of opportunity to absorb moisture from the atmosphere. The atmosphere in the Engine Test Bed room was very warm - over 25°C. Again different liquids were used to coat the deposits but even with water these deposits were far less susceptible to flaking compared to the previous three tests.

2.1.1.4 Test #25 – This test ran for 105 hours with Fuel E with 2.5 times the dose rate of the experimental additive AD10 used in Test #21. The engine was dismantled 20 hours after the end of test. There was very extensive flaking over all the piston and head surfaces. Deposits had come off the surface spontaneously in contrast to Tests 23 and 24 even though they had had a much shorter time to absorb ambient moisture at the end of the test compared to Tests 23 and 24. The temperature and humidity levels at the end of Tests 23 and 25 were comparable. Thus these deposits appear even more susceptible to deposit flaking compared to those from Test 23 which used AD10 at a lower dose rate. Figure 7 shows a piston-top (cylinder #3) from this test which shows such spontaneous flaking.

Water droplets were placed in different areas of the cylinder head and piston tops where the deposit had not peeled off. In general the droplets spread easily on the surface and deposits flaked 4-10 minutes later, the flakes often jumping off several centimetres as they came off.

2.1.1.5 Discussion of qualitative observations on deposit flaking – Thus not all combustion chamber deposits are equally susceptible to flaking. We can classify our

observations broadly into four classes of severity of flaking.

CLASS I - In some cases, the phenomenon is strong enough that deposits flake spontaneously by absorbing ambient water vapour. This had indeed been the case in Test 21 and also after the Test 25 as discussed above. The deposits shown could be easily removed by blowing on them.

CLASS II - In other cases, even though no spontaneous flaking was observed, the deposits reacted strongly and flaked a short time (4-6 minutes) after being coated with water sometime jumping several centimetres off the surface; this was the case in Test 23.

CLASS III - In some cases, the deposits are not hydrophilic at the end of the test and a drop of water placed on the deposited surface does not wet it. If the surface is wiped with a water soluble household detergent and then coated with water, the deposits again react vigorously and come off the surface a short time later. This happened in Test 22 as discussed above.

CLASS IV - Finally there are cases where the reaction with water is weak even after it wets the surface and deposit flaking is patchy and not very marked and takes significantly longer (40 minutes or over) where it occurs e.g. Test 24 above.

Thus the phenomenon is connected with the diffusion of water through the deposit. The difference in susceptibilities of deposits formed from different fuels/additives to flaking is partly related to how hydrophobic these deposits are. When a water droplet is placed on the deposit surface, there is a time delay before it diffuses to the relevant layer below the surface. Deposits then flake, some times with sufficient force to result in deposit flakes lifting off a few centimetres from the surface. It is not known if a chemical reaction is occurring between the deposits and the water. For example Lauer and Friel (8) speculated that acid anhydride groups may be responsible for adhesion of deposits to the surface and it may be these functional groups which react with the water. Alternatively, the water may simply bring about a physical disruption of the deposits releasing potential energy stored within the structure. However, getting the water to wet the top surface is a necessary but not sufficient condition to bring about deposit flaking. The hydrophilicity of the deposit surface which determines the penetration of water and the inherent susceptibility of the

relevant deposit layer to reaction with water both appear to be important in determining whether the deposit will flake.

2.1.2 Detailed analytical studies of deposits on the plugs - Several analytical techniques were used to study deposits on the plugs taken from Test #s 22 and 23. These studies were inconclusive and are described only briefly, mainly to underline the fact that the detailed mechanism by which flaking occurs is not clear.

X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) showed differences between the top and bottom surface of a deposit flake collected from Test #21 discussed above. For instance C=O and C-O bonds found in esters and anhydrides were much more abundant on the top surface than on the bottom surface of the flake. It is not clear whether this difference is the cause or the effect of interaction of the bottom surface with water. Mass spectroscopy showed no evidence of evolution of any gas when the flakes were soaked with water.

The deposit sample plugs were also studied using environmental scanning electron microscopy (ESEM) which is mainly used to study biological systems; the sample can be kept under saturated water pressure in the ESEM. The deposit morphology on a given plug varies and the features seen cover several of the generic types described in Ref. 9. In particular there were areas which showed deep cracks in the deposit surface. These cracks were opened up and the deposit flaked on exposure to saturated water vapour for twenty minutes in the ESEM. However it was not clear how exactly this came about. It is possible that the water ran along the cracks and forced the deposit apart or down the cracks to the metal/deposit interface before forcing the deposit flake upwards. It is also possible that the deposit swelled up on absorbing water and flaked as a result of internal pressures. It could also be due to water reacting chemically with critical layers in the deposit surface. However there was no strong evidence to support any one of these possible mechanisms relative to others.

All these analytical studies also showed that when deposits have flaked there is a thin layer of deposit still left on the metal surface. Thus the flaking is not necessarily due to the failure of the bonding between the metal surface and the deposit but due to weaknesses between different layers of deposits.

Table 3. Summary of Results for Different Fuels

FUEL + Additive	TEST NO	Max Mean Plug Deposit wt., W_{\max} (model), mg	TOTAL Test hours	Class of severity of flaking	F, Mean % Piston Surface Cleaned after flaking
E + AD10	23	25.6	111	II	80
E	24	35.5	105	IV	1
E + 2.5xAD10	25	23.5	105	I	95
E + AD3	26	39.2	105	IV	5
I	27	13.1	95.7	IV	1
F	28	23.0	95.6	IV	1.4
F + 12%v MTBE	29	20.0	90.7	IV	3
F + AD1	30	29.3	95.7	IV	0.5
I + AD1	31	14.6	90.7	IV	0.5
F + 10%v Ethanol	32	14.9	93	II	58
H	33	9.7	95	IV	8.5
H + AD1	34	25.0	95.6	IV	3
F + AD7	35	21.0	95.6	IV	13
F + AD1	38	29.3	90.7	IV	2.5
F + AD2	39	36.0	90.7	IV	0.75
F + AD4	40	22.2	90.7	IV	2.4
G	41	20.3	95	III to IV	14
F + AD9	42	28.8	90.4	III	20.2
F + AD9	43	28.8	90.6	III	38
G + AD1	44	29.7	89.6	IV	1.8
F + AD6	45	25.6	90.6	IV	7.4
F + AD3	46	26.2	90.4	III	31.5
F + AD5	47	29.0	89.6	IV	2.9
F + 12%vMTBE+AD1	48	22.5	75	IV	1.2
F + AD8	49	27.4	89.7	IV	16.5
I + AD1	50	14.6	85.1	IV	1
F + 10%v Ethanol + AD1	51	28.5	85	IV	4.3
F + 5%v Ethanol	52	34.1	90	II	80
F + 10%v Ethanol	53	14.9	85	II	75

Table 4 Summary of results from laboratory generated deposits

Test	Deposit mass	24 hour thermal treatment	Deposit mass after thermal treatment	Change in deposit mass	Elemental composition of deposit after thermal treatment			
	(mg)	(°C)	(mg)	(%)	C (%m/m)	H (%m/m)	N (%m/m)	O (%m/m)
1	82	none	82	0	59.6	5.2	1.0	34.2
2	99	100	90	9	58.1	5.0	0.9	35.9
3	93	150	74	20	62.6	5.0	1.1	31.3
4	91	200	54	41	61.3	3.6	1.1	34.0
5	80	250	33	58	60.5	2.4	1.5	35.6
6	93	300	12	87	60.0	2.1	2.7	35.2
7	87	350	1	99	n/d	n/d	n/d	n/d

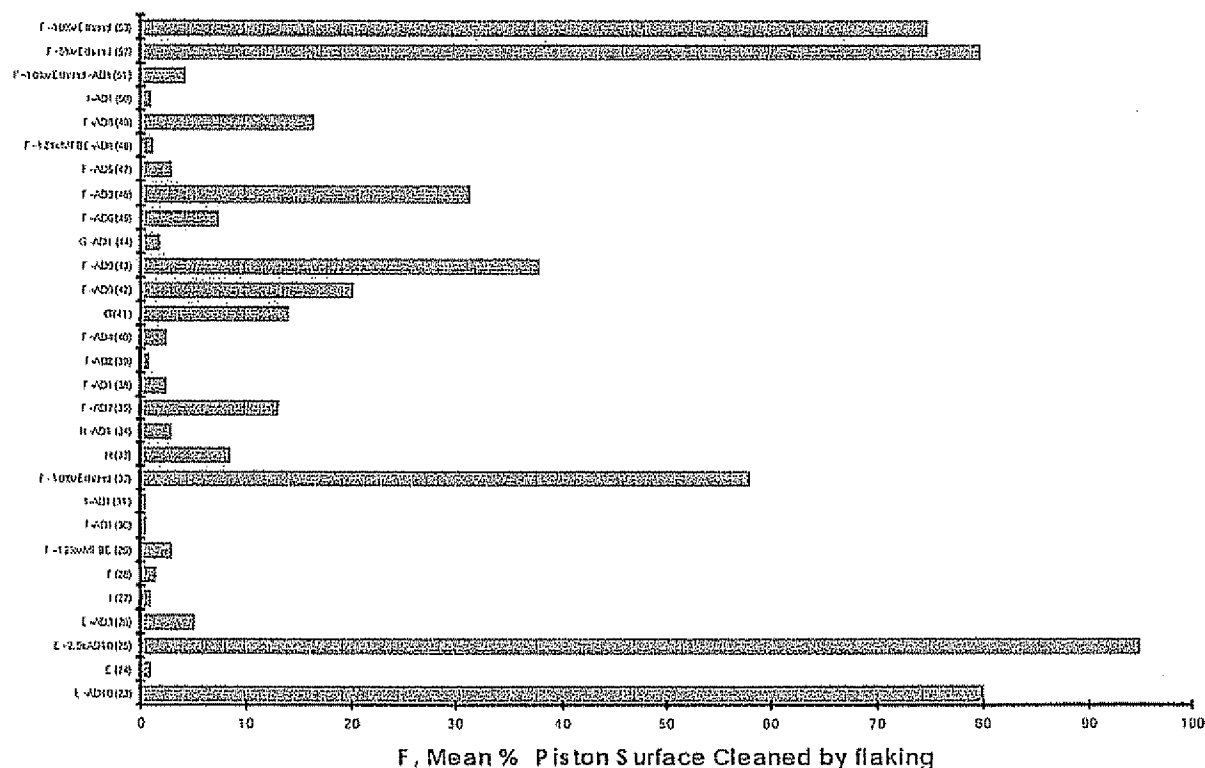


Figure 8. F, mean fraction of piston-top deposits removed at the end of a test after reaction with water. The test number (from Table 3) is shown in brackets for each test. There is a very wide range of flaking behaviour.

2.2.1 Experimental Detail – The surfaces of the rig are held at relatively low temperatures (70°C) compared to engine combustion chamber temperatures ($120^{\circ}\text{--}320^{\circ}\text{C}$) to allow for the rapid generation of deposit material. The deposits formed in the rig have the form of viscous liquids and are more representative of the material which forms during the early stages of deposit formation in engines. However, selective thermal treatment can be used to change the laboratory deposits into solids which have been shown to be physically and chemically similar to mature engine deposits (10). A range of thermal treatments have been used on deposits generated in the rig in order to test how the form of the deposit material affects water induced flaking.

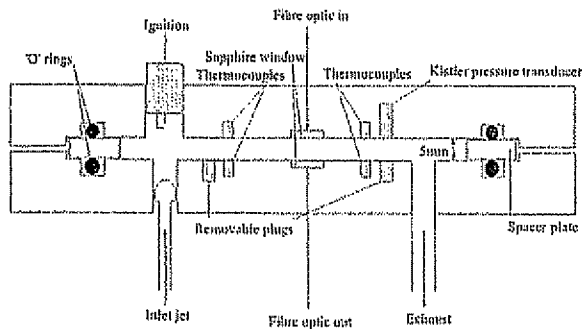
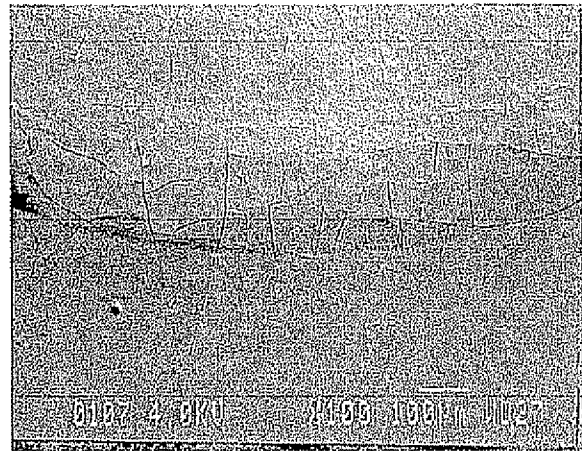


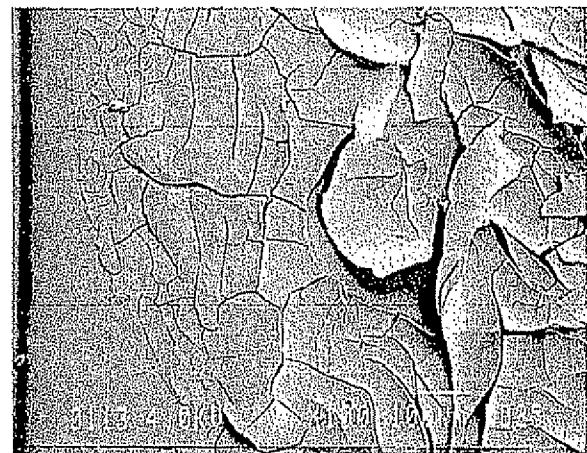
Figure 10. Schematic diagram of the laboratory quenched combustion deposit rig (surface-to-volume ratio=4cm⁻¹, Ignition - 8 sparks per second, surface temperature variable between 343-403K).

Deposits were generated from isopropyl benzene fuel, burned under stoichiometric conditions in the laboratory quenched combustion rig. At the end of each 5 hour test a sample stub, coated with deposit, was removed from the lower rig plate for flaking studies. The remaining deposit material was rinsed off the surfaces of the rig with methanol and evaporated to dryness. This bulk deposit and the sample stub were then dried in an oven for 24 hours at 50°C . This is the 'untreated sample' in the discussion below. The bulk deposit was then weighed.

The bulk deposit and the sample stub from each test were then thermally treated for 24 hours at temperatures ranging between 100° and 350°C . The bulk deposits were allowed to cool in a desiccator before re-weighing to determine the reduction in deposit mass. Elemental analysis was carried out to determine C, H, N and O composition for each sample. The sample stubs were also allowed to cool before applying a water droplet to one area of the deposit surface. The water was left to evaporate before studying the deposit films with a Scanning Electron Microscope.



(a) Micrograph of deposit sample on the stub dried at 50°C but without further thermal treatment. Shows extensive cracking but no flaking after interacting with water. The line across the middle of the picture marks the edge of the water droplet.



(b) Micrograph of deposit sample on the stub dried at 50°C and with further thermal treatment for 24 hours at 100°C . Shows extensive cracking and flaking after interacting with water. The line across the left hand side of the picture marks the edge of the water droplet.

Figure 11.

2.2.2 Results in the Laboratory Rig – Table 4 summarises the results from the seven tests. Thermal treatment leads to a reduction in the deposit mass (9% at 100°C increasing to 99% at 350°C), probably through a combination of evaporation of volatile species and thermal decomposition/ pyrolysis at higher temperatures. Although there are significant losses in deposit mass during each thermal treatment the elemental composition of the deposits showed only small variations. Hydrogen levels shift from 5% m/m in the untreated deposit to 2% m/m in the deposit treated at 300°C . Conversely,

nitrogen content increases from 1% m/m to 3% m/m over the same range. The carbon and oxygen contents fluctuate slightly between samples but do not show any clear trend with the temperature of the thermal treatment.

The thermal treatments produced a darkening in the colour of the deposit samples. The untreated sample was golden in colour whilst the sample treated at 300° C turned dark brown. There were however no visible differences in the surface texture of the deposits.

Only the water droplet applied to the untreated deposit material showed signs of wetting the surface; with all the other deposit samples, the droplets remained virtually spherical. As well as spreading, the droplet on the untreated deposit surface also appeared slightly cloudy, suggesting a degree of dissolution of deposit material from the surface below. After 10 minutes all the water droplets had evaporated to dryness leaving the deposit surfaces apparently unaltered except on the sample stub with deposits treated at 100° C. There was clear evidence of cracking and deposit flaking on this sample.

Under the Scanning Electron Microscope the untreated deposit, which had appeared featureless to the naked eye, showed extensive cracking in the area where the water had been applied (Figure 11a) but no flaking. The sample treated at 100° C is shown in Figure 11b revealing the full extent of the "damage" to the deposit film. The areas contacted by the water droplet have cracked, buckled and lifted from the underlying metal surface. The deposit sample treated at 150° C showed only a small degree of cracking around the edge of the area where the water droplet had been applied, but without any sign of flaking. For the samples treated above 150° C no cracking of the deposits was observed.

These results are consistent with observations of deposit flaking in Section 2.1 i.e. the phenomenon is dependent upon both the age of the deposit material and also its thermal history. The uniform elemental composition of all the sample tested in this work suggests that it is the physical form of the deposits that influences whether they flake when exposed to water. As the laboratory deposits were baked they changed from viscous liquids (which were lacquer-like) to solids. The untreated deposits were soft and underwent some cracking but no flaking when treated with water. The cracking and flaking seen after deposits were thermally treated at 100° C probably occurs because the material is more solid-like and brittle in nature. The higher thermal treatments would appear to leave the deposits hard and resistant to water.

3. ROAD TEST PROCEDURE

We have developed a 3000 mile road test which focuses on assessing the susceptibility of deposits formed from a given fuel to flake. At the end of each test, the deposit thicknesses on piston tops are measured in detail. The

piston-tops are then sprayed with water, sufficient time is allowed for any flaking to occur, the flakes are removed by blowing on the piston tops and the deposit thicknesses measured again. The average ratio of deposit thickness after this treatment to the deposit thickness before the treatment is taken to be a measure of the susceptibility of flaking - the lower this average, the worse the flaking. The test has proved itself to be sensitive and capable of differentiating clearly between different fuels in terms of deposit flaking. It has also confirmed most of the observations described in this paper. This test can be used to assess different fuel and additive combinations. It will be described and the results reported at a later date.

4. CONCLUSIONS

1. Combustion chamber deposits can flake by interacting with water, which is present in the atmosphere and in the gases in the cylinder from previous combustion, when the engine is not running. Water is far more effective than fuel or other organic solvents in causing such flaking.
2. There is a wide variation between different fuels and additives. Conventional detergent additive packages suppress flaking whereas some experimental additives can promote flaking.
3. Deposit flaking depends on the temperature regime under which the deposits are formed. Thus fuels which might produce deposits which do not flake in one engine (or operating regime) might produce deposits which flake in another engine (or operating regime) with a different thermal environment.
4. "Young" deposits do not flake. They probably need to build up sufficient thermal stress in the relevant layers before they can flake.
5. There is no correlation between the deposit level i.e. weight or thickness and the susceptibility to flake.

The hydrophilicity of the deposit surface which determines the penetration of water and the inherent susceptibility of the relevant deposit layer to reaction with water are both important. Conventional detergent additive packages probably make deposits less permeable to water and so reduce their susceptibility to flake. The type of flaking described in this paper could cause problems associated with deposit flakes propping open exhaust valves.

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